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DYNAMIC DIFFERENTIAL CALORIMETRY OF INTERMETALLIC COMPOUNDS

I. HEAT OF FORMATION, HEAT AND ENTROPY OF FUSION OF RARE EARTH–TIN COMPOUNDS

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ABSTRACT

Dynamic differential calorimetry has been employed to evaluate the heats of formation, heats and entropies of fusion of $RESn_3$ compounds, where rare earths (RE) = La, Ce, Pr, Nd, Sm, Gd, Eu, Yb and Ca. The results obtained have been estimated to be correct to within ±5–6%. The agreement between these values and those obtained from other authors can be taken as an indication of the reliability of the method.

INTRODUCTION

The crystal structures and the lattice constants of many rare earth (RE) intermetallic compounds are well established but in most cases their thermodynamic properties are not known. We have therefore developed a method suitable for the direct determination of the heats of formation and heats of fusion based on using a conventional differential thermal analysis apparatus. If the heat of formation of a compound can be measured by a reaction involving direct combination of the elements the result is likely to be more accurate than if an indirect method is employed. Another advantage of this method compared with other traditional techniques is the speed with which the measurements can be carried out: a single determination taking no more than one or two hours.

The method of dynamic differential calorimetry (DDC), first described in 1958, has received a satisfactory theoretical treatment by Faktor and Hanks[1] who used this method to evaluate the heats of formation of rare earth alloys[2].

Briefly, the sample and the reference material (a one gram ingot of Mo), are placed in two molybdenum containers with covers, which rest on two differential thermocouples, supported by alumina rods. The whole is enclosed by an alumina cap and a third thermocouple between the crucibles records the temperature of the enclosure (Fig. 1). Following the theory develop by Faktor and Hanks the sensitivity (S) of DDC, *i.e.* the peak area produced by unit enthalpy change in the sample, can be written as follows

$$\frac{1}{S} = \frac{\Delta H}{\int_0^t \Delta T \, dt} = A + BT_m^3$$

where

ΔH = enthalpy change in the sample,

$\int_0^t \Delta T dt$ = peak area,

A, B = constants containing the transmission coefficient for conduction and radiation, and

T_m = temperature of the central thermocouple at which the peak area can be divided into equal parts (see Fig. 4).

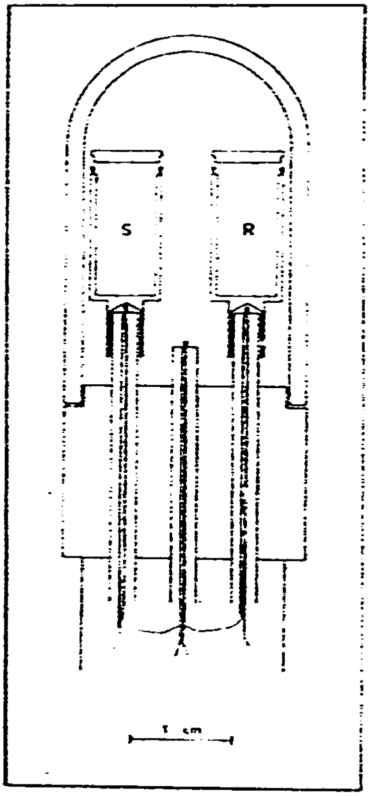

Fig. 1. Crucible assembly for dynamic differential calorimetry. S = sample, R = reference.

We have tested such a theory in the temperature range 200–1100 °C and have applied the DDC method to $RESn_3$ compounds. These phases have been chosen first of all because tin reacts easily at low temperature with RE's—the reaction is highly exothermic and the heat evolved is sufficient to melt the sample; secondly, because the heats of formation of some $RESn_3$ compounds have been measured by other authors using using methods, and their results supplies a test for the reliability of the method itself.

EXPERIMENTAL

Apparatus

The apparatus used was a conventional DTA equipment obtained from Netzsch (West Germany) of the same type as that used by Faktor and Hanks in their investigation. Crucibles and covers were of molybdenum which is inert in respect to tin and rare earths. A two-point recorder gave simultaneous plots of the differential temperature and the temperature of the enclosure. The operating atmosphere was ultra-pure argon. The furnace could be programmed for linear heating rates from 0.1 to 100 deg/min up to 1500°C. Thermocouples were Pt/Pt–10% Rh.

Procedure

Calibration curves were obtained using elements and compounds of known heats of fusion in the temperature range 200–1100°C and their values are reported in Table I. For each substance samples corresponding to thermal effects of 25–30 cal were employed and only fusion peaks were considered. The furnace was heated at 10 or 20 deg/min and each substance was tested four times. The peak areas were determined by a planimeter so that the reciprocal sensitivity was espressed in cal/cm^2; Fig. 2 reports a plot of these values against temperature.

TABLE I

REFERENCE MATERIALS

Substance	*Melting point (°C)*	*ΔH (kcal/mole)*	*Reference*
Sn	232	1.645±0.016	5
Bi	271	2.755±0.018	5
Cd	321	1.530±0.04	3
Zn	420	1.755±0.020	5
Sb	631	4.690±0.1	4
Mg	650	1.970±0.016	5
NaCl	801	6.7 ±0.1	3
Ag	961	2.650±0 1	3
Au	1063	3.05 ±0.1	3
Cu	1083	3.1 ±0.1	3

The reciprocal sensitivities in cal/cm^2 were converted into cal/deg min as required by the theoretical analysis by using the three conversion factors: recorder sensitivity (cm/μV), thermoelectric power of the thermocouple at the temperature in question (μV/deg) and chart speed (cm/min). Thus a plot of $1/S$ against T_m^3 (Fig. 3) appears linear as the theory requires; the equation obtained using least-squares analysis is

$$1/S = 8.48 + 1.1009 \times 10^{-6} T_m^3 \text{ cal/deg min.}$$

In the evaluation of the heats of formation and heats of fusion, single curves for 10 and 20 deg/min were employed.

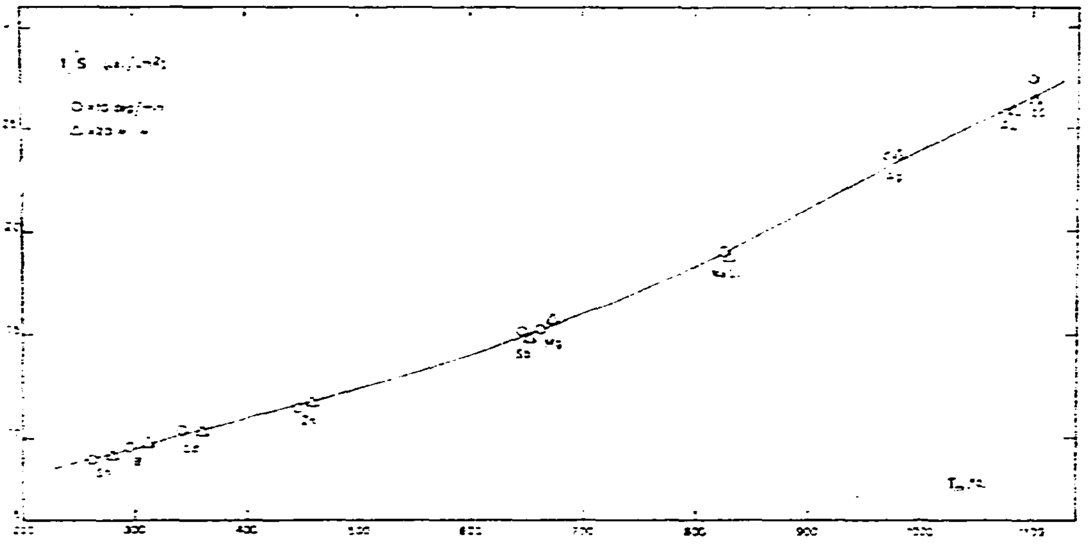

Fig. 2. Variation of reciprocal sensitivity with temperature.

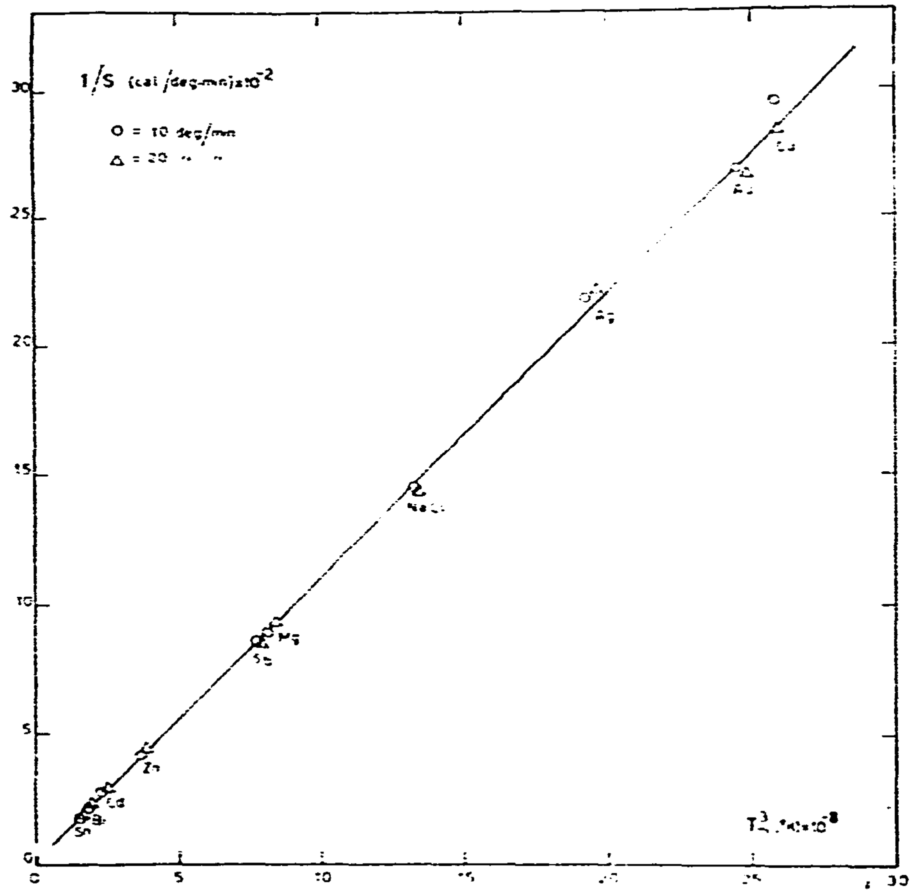

Fig. 3. Reciprocal sensitivity against the cube of the absolute temperature.

Errors

The major source of errors in the calibration curves lies in the existing discrepancies in the values of the heats of fusion for the reference materials. From the examination of the literature data[3–10] it appears evident that for a certain element the known values of the heat of fusion differ from one another by ±3–5% at least, each one being known with an accuracy of ±1–3%. Therefore the maximum error introduced from calibration curves and from standard points was estimated to be ±4%. The values reported in Table I were selected from a critical survey of the known data and correspond in most cases to the most recent determination.

$RESn_3$ COMPOUNDS

$RESn_3$ compounds are well known structurally[11,12] and some of them have been recently investigated determining their heats of formation[13–16]. RE metals and tin used in this research were obtained from Koch–Light Laboratories, England, and had a purity of 99.9 and 99.999% respectively. Samples ranging from 0.75 to 1.00 gramme each were prepared from stoichiometric amounts of powders of the two metals (50 mesh) well mixed and pressed directly in the Mo containers (1.5 KBar).

The reaction between RE and liquid tin starts at low temperature, is very fast for the lighter RE (La, Ce, Pr) and the thermal effect due to the melting of tin must be considered in the evaluation of the heat of formation of the corresponding compound. The other RE (Nd, Sm, Gd) react at higher temperature and the two thermal effects, *i.e.* melting of tin and heat of reaction, are widely independent. Typical examples are reported in Fig. 4 for La and Gd. To ensure reproducibility in the

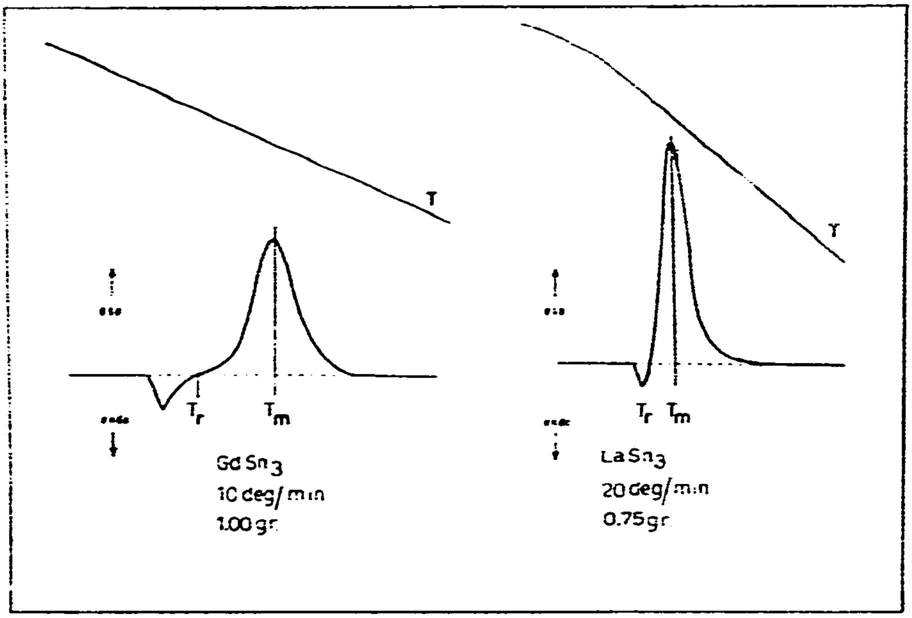

Fig. 4. Examples of thermograms obtained for the reaction between rare earths and tin.

results, several samples for each heating rate were prepared and at least two "good" samples were considered in the evaluation of the heats of formation. Table II reports the values obtained, with different heating rates, compared with those reported in the literature.

TABLE II

HEATS OF FORMATION (in kcal/mole) FOR $RESn_3$ COMPOUNDS

Comp.	T_r[a] (°*K*)	ΔH_{form}					*Ref.*
		(10°C/min)	*(20°C/min)*	*(mean val.)*	*(298°K)*	*(Lit. values)*	
$LaSn_3$	510	−64.60	−65.76	−65.18	−60.25	−60.60 (273°K)	13
$CeSn_3$	510	−53.73	−54.29	−54.01	−49.08	—	—
$PrSn_3$	520	−62.25	−59.49	−60.87	−55.94	—	—
$NdSn_3$	520	−72.62	−69.16	−70.89	−65.96	—	—
$SmSn_3$	570	−58.06	−58.90	−58.48	−53.55	−53.80 (295°K)	14
$GdSn_3$	600	−53.23	−54.21	−53.72	−48.78	−49.65 (299°K)	16
$YbSn_3$	540	−51.24	−50.36	−50.80	−45.86	−42.10 (294°K)	15

[a] T_r = temperature at which the reaction starts.

After the reaction has ended the samples were examined micrographically: all of them were single phase and only in the case of $YbSn_3$ about 1 or 2% of another phase was observed. Attempts to prepare $CaSn_3$ and $EuSn_3$ (isomorphous with the other $RESn_3$ compounds) failed, giving non-homogeneous products.

X-ray examination showed the presence of the $RESn_3$ phase with no extra lines due to other phases or to unreacted metals. The values of the lattice constants are in good agreement with literature values.

As the heats of formation are obtained at different temperatures, they were reported, by means of the Kirchoff's relation, at 298°K corresponding to the reaction:

$$RE(s)+3Sn(s) = RESn_3(s)+\Delta H_f$$

The calculations would imply a knowledge of the heat capacities for RE, liquid and solid tin and for the compound but, if nothing whatever is known about the heat capacity of the compound, assuming the validity of the Neumann and Kopp's rule, ΔC_p may be considered to be zero for condensed reactions without affecting the results too much and especially in this case where the ΔT is small[3]. The heats of formation were therefore corrected only for the heat of fusion of tin and the values so obtained are reported in Table II. Assuming a total error of ±5–6% for our values we observe good agreement with those obtained by other authors who use different methods.

Heats and entropies of fusion of $RESn_3$ compounds were determined by preparing a new series of one gram samples, and sealing them by arc welding under argon atmosphere in Mo crucibles; this procedure is necessary to avoid losses of metals (Sm, Yb, Eu, Ca) at high temperature via sublimation. At the melting points of the alloys, which are in good agreement with the known values, the heats of fusion were determined by means of the calibration curves and hence the entropies of fusion were calculated; these values are reported in Table III. From the DTA curves it is also possible to observe that all $RESn_3$ compounds examined have similar melting poin[illegible]cept $GdSn_3$ which is formed peritectically. Table III also reports the values for [illegible]$_3$ and $EuSn_3$ which also have again similar melting points.

TABLE III

HEATS AND ENTROPIES OF FUSION FOR $RESn_3$ COMPOUNDS

Compound	T_f (°C)	ΔH_f (*kcal/mole*)	ΔS_f (*cal/deg mole*)
$LaSn_3$	1138	11.50	8.15
$CeSn_3$	1160	16.45	11.45
$PrSn_3$	1155	18.01	12.61
$NdSn_3$	1138	17.67	12.52
$SmSn_3$	1072	15.95	11.86
$EuSn_3$	784	10.14	9.59
$YbSn_3$	805	15.30	14.19
$CaSn_3$	625	10.79	12.02

DISCUSSION

Rare earths, from La to Gd with Eu and Yb, form with tin $RESn_3$ phases which crystallize with the $AuCu_3$ type of structure. Eu and Yb in these compounds behave like alkaline-earth elements containing Eu^{2+} and Yb^{2+} in accordance with the existence of $CaSn_3$ isomorphous with them.

From the thermodynamic data obtained it can be seen that the general trend is a decrease from La to Gd in the heats of formation and this fact agrees with the decrease in the heats of solution of rare earths in liquid tin[13–18]. In considering the value for $CeSn_3$ one must remember its anomalous magnetic properties, the valence of Ce in $CeSn_3$ at room temperature being[19] about 3.3. Finally the high heat of formation of $NdSn_3$ would indicate a greater stability of this compound in respect to the other $RESn_3$ phases.

The results obtained in this research lead to the conclusion that the DDC method can be employed with reasonable confidence in the determination of the heats of formation and heats of fusion of intermetallic compounds. The method appears to prove itself competitive with other traditional techniques both for the total error which affects the results (±5–6%) and for the speed and ease of operation. Unfortunately only highly exothermic and fast reactions, which lead to the complete formation of the desired compound, can be examined.

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